Message

From: Detlef Knappe [knappe@ncsu.edu]
Sent: 12/1/2017 1:26:28 PM
To: Michael Pjetraj [michael.pjetraj@ncdenr.gov]; michael.abraczinskas@ncdenr.gov; Culpepper, Linda [linda.culpepper@ncdenr.gov]; James Bowyer [jim.bowyer@ncdenr.gov]; Gary Saunders [gary.saunders@ncdenr.gov]
CC: Strynar, Mark [Strynar.Mark@epa.gov]; Lindstrom, Andrew [Lindstrom.Andrew@epa.gov]; Graham Peaslee [gpeaslee@nd.edu]; Mei Sun [msun8@uncc.edu]
Subject: [SPAM-Sender] Re: [External] Chemours sampling

Thank you, Michael! Is the goal to measure the PFAS composition leaving the stack, which may contain a mixture of different acid fluorides and their PFECA counterparts, or the PFECA formation potential of the compounds leaving the stack by converting the acid fluorides to their respective acids during sampling/sample extraction from the sorbent?

Based on the well data, it appears that 4, 5, and 6-carbon acid fluorides are being emitted in substantial quantity into the atmosphere.

Currently, we have quantitative analytical methods for the PFECAs (e.g. PFMOPrA, PFMOBA, GenX), but not for the corresponding acid fluorides.

I will assemble a few papers on ambient air sampling protocols for PFASs over the weekend and send to you.

Best,

Detlef

On 12/1/17 6:36 AM, Pjetraj, Michael wrote:

Dr. Knappe,
Thanks for your message. Please see the information below.

I am interested to learn more about the planned stack sampling. What analytical methods will be employed? Targeted? Non-targeted? Would the sample collection approach for stack sampling lend itself to determining total fluorine? If polyurethane foam plugs are used, we could use them directly for PIGE (as mentioned by Graham, this could be done in a non-destructive manner), and extracts from PUFs could be used for high resolution MS, total oxidizable precursor test, and adsorbable organic fluorine.

Proposed Stack Testing for GENX compound - The test methodology proposed is a modified Method 0010 from the EPA SW-846 series of test methods. Gas is drawn into the sampling train at an isokinetic rate for capture and analysis The method is described in SW-846 as a modified EPA Method 5 particulate test method that includes a resin adsorbent tube for certain organic compounds that pass through the filter as a gas and, upon cooling through a condenser, may be either a gas or liquid when it passes through the resin tube. However, an additional modification is the use of an additional tube (in series) for recovery before the gas passes into and through the impingers. The temperature of the sampling must be controlled within a range to prevent condensation in the probe and filter but also prevent chemical breakdown due to temperature.

Upon completion of sampling, the sample is recovered from the probe, filter, adsorbent tubes and impingers. The analytical methods include extraction from the collected samples and use of LC/MS/MS to determine the presence and concentration levels of GENX captured by the sampling train. We anticipate that only the C3 dimer acid will exist due to the reactivity of any dimer acid fluoride with water. Other polyfluorinated compounds may be recovered and detected by this methodology. However, GenX is the target pollutant for measurement. The facility is not planning on quantifying total fluorine at this time.

I am also interested to learn more about the planned ambient air monitoring. I have never done such monitoring in my group, but Morton Barlaz (my Department Head), Mei Sun, Mark, Andy, and I have a proposal out to begin such efforts to determine PFAS levels in ambient air around landfills.

We have been in conversations with EPA on ambient monitoring, but we have not committed to a plan at this time. We are exploring rain collection sites and associated analysis. We have also spoken with Dr. Mead at UNCW on rainwater analysis.

Please let me know if you would like to discuss any of this information further or have additional questions. I can be available for a call today. Mike Abraczinskas will be at the SAB meeting in Wilmington on Monday & I will be at the conference at UNCW on 12/11.

Sincerely,
Michael

Michael Pjetraj, P.E.
Deputy Director
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North Carolina Department of Environmental Quality

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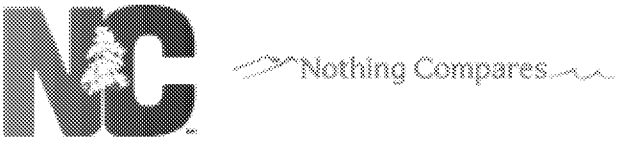

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Friday, November 10, 2017 11:40 PM
To: Abraczinskas, Michael <michael.abraczinskas@ncdenr.gov>; Culpepper, Linda <linda.culpepper@ncdenr.gov>; Pjetraj, Michael <michael.pjetraj@ncdenr.gov>; Bowyer, Jim <jim.bowyer@ncdenr.gov>; Saunders, Gary <gary.saunders@ncdenr.gov>
Cc: Strynar, Mark <Strynar.Mark@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Graham Peaslee <gpeaslee@nd.edu>; Mei Sun <msun8@uncc.edu>
Subject: Re: [External] Chemours sampling

Somewhat long email - please read all the way.

Mike,

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total fluorine? If polyurethane foam plugs are used, we could use them directly for PIGE (as mentioned by Graham, this could be done in a non-destructive manner), and extracts from PUFs could be used for high resolution MS, total oxidizable precursor test, and adsorbable organic fluorine.

I am also interested to learn more about the planned ambient air monitoring. I have never done such monitoring in my group, but Morton Barlaz (my Department Head), Mei Sun, Mark, Andy, and I have a proposal out to begin such efforts to determine PFAS levels in ambient air around landfills.

All,

It sounds like air samples should be done at a later time. How about we first start with water samples as mentioned below? In that case, I am thinking:

1. Mark Strynar - High resolution MS (2 L from each location)

2. Athens lab (2 L from each location)

3. Mei Sun's lab - Adsorbable organic fluorine (2 L from each location)

4. Knappe group - (1) Total oxidizable precursor (TOP) assay, (2) solid phase extraction of original sample, and (3) solid phase extraction of sample following TOP assay. Then send (2) and (3) to Graham Peaslee's lab for PIGE analysis (4 L from each location)

That's 10 L from each location - could all be collected in 1-L HDPE bottles.

Sampling locations: 001, 002, groundwater well on Chemours property, old waste ditch, Huske Dam

That would take 50 bottles in total (5 sampling locations, 10 bottles each).

Linda,

When could such samples be collected?

I also wonder whether we could include one of the private wells and a lake near Chemours in the Marshwood Lake area. I talked to one resident, whose well has >500 ppt GenX, and her lake has >900 ppt GenX. The latter results would help inform stack sampling and ambient air monitoring programs.

Thank you,

Detlef

On 11/3/17 9:04 AM, Abraczinskas, Michael wrote:

Thanks for looping us in Linda!

DAQ continues to discuss/explore appropriate methods for ambient air quality monitoring... however, in the very near-term, we are more focused on source emissions characteristics, chemistry and stack testing methods.

We believe the better we understand the process chemistry and behavior (chemical and physical transformations) of the various compounds when they roll off the lip of the stack into the atmosphere... the better we'll be able to design an exploratory ambient monitoring approach with a defined goal, analytical methods, analytes of interest... and all of the other elements of a scientifically sound sampling plan.

We are meeting with Chemours on Tuesday, 11/7 to further explore the process chemistry and stack testing. In fact, Chemours submitted a stack testing protocol to us on 10/31 and our staff are currently reviewing that. As we understand it now, Chemours wants to conduct the stack tests before the end of the year. My hope is the stack test results will help refine the magnitude and rate of air emissions... which at this point are only estimated by Chemours via a model or engineering estimates.

Back to ambient monitoring... I think we would all benefit from a coordinated approach to any ambient air quality monitoring and welcome all knowledge, information, resource sharing & opportunities for collaboration. I'm looping in

our lab supervisor, Jim Bowyer, to this email and ask that he be part of all discussions regarding ambient air quality monitoring.

Thanks everyone!
-Mike

Mike Abraczinskas, EIT, CPM
Director, Division of Air Quality
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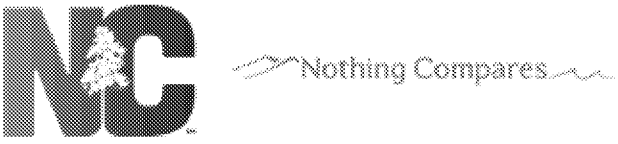

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Friday, November 03, 2017 8:15 AM
To: Culpepper, Linda <linda.culpepper@ncdenr.gov>; Abraczinskas, Michael <michael.abraczinskas@ncdenr.gov>
Cc: Strynar, Mark <Strynar.Mark@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Graham Peaslee <gpeaslee@nd.edu>; Mei Sun <msun8@uncc.edu>
Subject: Re: [External] Chemours sampling

Thank you, Linda!

Mike,

What are your plans for air quality monitoring around the Chemours plant. Locations? Schedule?

Best,

Detlef

On 11/3/17 7:40 AM, Culpepper, Linda wrote:

Looping Mike, our Air Quality Director, into our email thread.

Linda Culpepper
Deputy Director
Division of Water Resources
North Carolina Department of Environmental Quality

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Phone: 919-707-9014

From: Mei Sun [mailto:msun8@uncc.edu]
Sent: Wednesday, November 01, 2017 10:44 AM
To: Detlef Knappe <knappe@ncsu.edu>
Cc: Strynar, Mark <Strynar.Mark@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Graham Peaslee <gpeaslee@nd.edu>; Culpepper, Linda <linda.culpepper@ncdenr.gov>
Subject: Re: Re: [External] Chemours sampling

I think this plan is great. I surely could do AOF in aqueous samples, not quite sure about air samples, but could try a solvent extract of the air filter (my guess is water extract of the air filter would have too low concentration to be detected but also worth a try).

Mei Sun

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Website: https://coefs.uncc.edu/msun8/

On Wed, Nov 1, 2017 at 9:42 AM, Detlef Knappe <knappe@ncsu.edu> wrote:

> Mei, Graham, Mark, and Andy,
>
> Please see my email to Linda Culpepper below about an idea for a small study to assess total organic fluorine in Chemours wastewater and impacted surface water. We could generate a challenge sample in the lab that could serve as a control.
>
> Let me know what you think.
>
> Best,
>
> Detlef
>
> -------- Forwarded Message --------
>
> **Subject:**Re: [External] Chemours sampling
> **Date:**Wed, 1 Nov 2017 13:16:20 +0000
> **From:**Culpepper, Linda <linda.culpepper@ncdenr.gov>
> **To:**Detlef Knappe <knappe@ncsu.edu>
>
> The below sounds like a good pathway. We could get samples from all of the areas.
>
> Sent from my iPhone
>
> On Nov 1, 2017, at 8:18 AM, Detlef Knappe <knappe@ncsu.edu> wrote:

Hi Linda,

I reached out to Graham Peaslee and Mei Sun yesterday. If you like, I could organize a small, coordinated study that explores the various analytical approaches for total organic fluorine on (1) a lab-generated standard into which we spike a mixture of PFASs (as a control) and (2) one or more field samples (e.g. 001, 002, old waste ditch, and/or Huske Dam). These samples would be split as follows:

1. Mark Strynar - High resolution MS

2. Athens lab

3. Mei Sun's lab - Adsorbable organic fluorine

4. Knappe group - (1) Total oxidizable precursor (TOP) assay, (2) solid phase extraction of original sample, and (3) solid phase extraction of sample following TOP assay. Then send (2) and (3) to Graham Peaslee's lab for PIGE analysis

What do you think? Which samples would be of interest?

Best,

Detlef

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